

TITLE: ENVIRONMENTAL CONTROL TECHNOLOGY FOR COAL CLEANING WASTES

MASTER

AUTHOR(S): P. Wagner, R. C. Heaton, L. E. Wangen, A. M. Nyitray,
M. M. Jones

SUBMITTED TO: Proceedings of a Workshop on Processing Needs and Methodology
for Wastewaters from the Conversion of Coal, Oil Shale and
Biomass to Synfuels, June 1981, Germantown, MD

DISCLAIMER

By acceptance of this article, the publisher recognizes that the
U.S. Government retains a nonexclusive, royalty free license
to publish or reproduce the published form of this contribu-
tion, or to allow others to do so, for U.S. Government pur-
poses

The Los Alamos Scientific Laboratory requests that the pub-
lisher identify this article as work performed under the aus-
pices of the U.S. Department of Energy

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663 Los Alamos, New Mexico 87545

An Affirmative Action/Equal Opportunity Employer

ENVIRONMENTAL CONTROL TECHNOLOGY
FOR
COAL CLEANING WASTES

P. Wagner, R. C. Heaton, L. E. Wangen,
A. M. Nyitray and M. M. Jones
Los Alamos National Laboratory
Los Alamos, NM 87545

INTRODUCTION

Mineral wastes from coal preparation and mine development constitute a major environmental problem. More than three billion tons of these materials have accumulated in the U. S. and the current annual production exceeds 100 million tons. The total number of coal waste dumps is estimated to be between 3000 and 5000, of which half pose some type of health, environmental or safety problem. As part of an effort to address these problems we initiated a research program at the Los Alamos National Laboratory several years ago with the ultimate aim of delineating solutions to control of the drainages from coal waste piles.

In the pursuit of this program we have adopted a general and straightforward approach to the solution of this type of problem. Coal waste samples were first thoroughly characterized both chemically and mineralogically. Then they were leached with water and the compositions of the resulting leachates determined. With this information we were able to develop an understanding of the environmental behavior of the coal wastes. The exact natures of the problems were determined and their sources and causes evaluated. With this as a basis, solutions to the problems were devised and evaluated. This approach is applicable to virtually any water pollution problem. In addition it provides a substantial data base which will ultimately lead to the development of a predictive capability as regards the environmental behaviors of solid wastes. In the following discussion we shall briefly touch the highlights of our coal waste program and show how this approach has lead us to the various control options which we suggest.

DISCUSSION

Let us consider first the leachates. Figure 1 shows in a simplistic manner the results of analyses for fifty elements in the leachates from high

sulfur coal wastes from plants in the Illinois basin. Elements whose symbols are circled are those elements which were determined. The ones which are shaded in black are those whose concentrations exceed the adjusted MATE¹ values and which may be cause for environmental concern. This chart clearly shows that the coal waste effluents are acidic (high H⁺ concentration) and that the trace elements of environmental concern are aluminum, a number of first row transition metals, arsenic and cadmium. This is not to say that these exact elements are always present in large amounts in all coal waste drainages, but rather that these tend to occur in environmentally significant amounts in the majority of cases.

Table 1 lists the discharge severities of the more important elements according to the MEG/MATE evaluation. The discharge severities were calculated by dividing the concentration of the respective elements in the leachate by one hundred times the ecology MATE¹ value for that element. Our experiments show that these leachates can be very acidic, sometimes having pH values less than two. The elements with the highest discharge severities are iron, nickel, manganese and aluminum in approximately that order, although this order varies depending on the coal waste. Most of these elements are not appreciably soluble in water at neutral pH values and are mobilized as a direct consequence of the high acidity of the leachates. It would seem at the outset that control of the acidity would largely control the effluent quality and this historically has been the approach used to solve this problem.

Table 2 shows the results of mineralogical analyses of coal wastes from five coal preparation plants located in the Illinois basin and in Appalachia. There are three outstanding features which one should note. First, all of the wastes contain large amounts of pyrite and marcasite. These minerals, when oxidized, give rise to sulfuric acid and ferrous sulfate and thus are the source of the two major components in coal waste drainages. Second, all of these wastes contain little or no carbonate minerals (calcite) and thus have little capacity to neutralize the acid once it is generated. Finally, all of these wastes contain substantial amounts of clay minerals. We have amply demonstrated through our past work that most of the leachable trace elements

¹ A dilution factor of 100 was applied to the MATE values at the recommendation of Garrie Kingsbury of RTI, who is one of the authors of the MEG/MATE evaluation system.

reside in the clay fractions of the wastes.¹⁻³ Consequently the presence of large amounts of clay minerals indicates that these wastes all have large reservoirs of leachable trace elements. In summary, the mineralogy shown by these mineral wastes is a prescription for undesirable effluent quality. All contain a strong acid generating potential with little or no self-neutralizing capability and a large reservoir of leachable trace elements.

Having gained the knowledge of coal waste effluent composition and the causes thereof, one can go about devising strategies for controlling these effluents. One way is to alter the waste in such a way that its acid generating capability is eliminated and/or the leachable trace elements are immobilized within the waste. A second way is to add materials to the waste in order to neutralize the acid as it is generated and before it can give rise to an acid leachate. A third approach is to collect the leachates and treat them before discharging them into the environment. In our research program we have evaluated techniques based on each of these approaches. In the interest of brevity we shall limit this discussion to the most effective in each category.

Let us first consider alteration of the waste. One may recognize this as a direct attack on the source of the problem, which is usually the most desirable course provided it can be achieved at a realistic cost. Unfortunately the waste composition must be altered in a rather fundamental way, which means that a great deal of work must be done in order to accomplish this. The most effective way which we have found to do this is to calcine the wastes. This involves heating the waste to high temperatures (1000°C) in order to bring about fundamental changes in the waste structure. The result of this treatment is to drive off the sulfur, which eliminates the acid generating potential of the waste, and to sinter some of the other minerals present, which should help to immobilize the trace elements present in them. Table 3 shows the trace element leachability of calcined and uncalcined wastes. Two things are clear. First, the pH of the leachate from the calcined refuse is neutral (8.0) and, second, the trace element concentrations of the leachate from the calcined wastes are drastically lower than those from the uncalcined wastes. Figure 2 shows the same data expressed as discharge severities. The calcining treatment is clearly quite effective in controlling the effluent quality. This treatment has the additional advantage of being a one-time treatment. That is, once the waste has been so treated, it need never be of environmental concern again. However, there are two severe disadvantages. One must deal somehow with the

large amounts of evolved sulfur compounds and also with evolved volatile trace elements. Even more important, however, is the high cost associated with this process. We shall have more to say about costs later.

The second approach to dealing with the coal waste effluent problem is to add materials to the coal waste which will either neutralize the acid as it is formed within the pile, or which will absorb the trace elements as they are leached. While this approach does not confront the source of the problem directly, it does seek to deal with the consequences of the problem source before they develop into a major problem. While we have investigated a variety of materials for codisposal with coal waste, the best system so far is a sequential slurry coating of the coal waste with hydrated lime and then powdered limestone. The lime serves to neutralize the initial acidity present in the waste. While the lime is effective for this, the excess lime is quickly washed out of the pile so that it is ineffective in dealing with acid generated within the pile at a later time. On the other hand, the limestone is not very soluble in water and remains in the waste pile for long periods of time. Consequently it is effective in controlling the acid which is slowly generated over time, but not very effective in neutralizing the large amounts of acid which are sometimes initially present. Use of these two materials together has proven to be a good way to control the effluent quality. Figure 3 shows the results of an artificial weathering experiment carried out on a sample of high sulfur coal waste treated sequentially with 0.35 percent lime and 1.1 percent limestone. This clearly shows the effectiveness of this treatment during the earlier part of the experiment. The pH is maintained within the range of 7.0 to 7.5 for a period of more than sixteen weeks before the system breaks down. After this time the pH drops to values typical of untreated coal wastes (approximately 2). Figure 4 shows the concentration of iron in the leachate as a function of time for the same experiment. Early in the experiment the iron concentration was always near the detection limit and well below the level at which one needs to be concerned. In fact it was not until nearly twenty weeks into the experiment that the discharge severity for iron reached unity. All of the other trace elements showed similar behaviors. These are shown in Figure 5. Figure 5 shows a comparison of the discharge severities of a number of selected trace elements from untreated and lime/limestone treated coal wastes. Discharge severities are used here instead of concentrations because the former expression give a better idea of the significance of an

elemental discharge than the later. In all cases the discharge severities for the treated wastes are less than unity, which indicates that this effluent is probably environmentally safe with respect to each of these elements. Note that a number of elements have very large discharge severities for the untreated wastes. The most extreme case is that of iron, which has a discharge severity of nearly 500 in the untreated waste, but less than 0.02 in the lime/limestone treated waste. On the basis of these data, one must conclude that the lime/limestone slurry coating treatment is highly effective in controlling the pH and the trace element contents of coal waste effluents.

The obvious limitation of the lime/limestone treatment in its present form is that it is not permanent. However we achieved four months of adequate control with an experiment designed to test a concept, with no attempt at optimizing the conditions.^{4,5} Presumably the length of the control can be improved with appropriate development work. Such an improvement would not, however, solve the basic problem, which is to provide a permanent solution to the coal waste effluent problem. We feel that the lime/limestone treatment will most likely find its place as one part of a more comprehensive control system, which might ultimately include returning the coal waste to its original anaerobic environment. The non-oxidizing environment would provide the permanent control, while the lime/limestone treatment would provide the temporary control while the anaerobic conditions can be established.

In summary, the lime/limestone slurry coating treatment combines a number of advantages. First, it is simple, since it can be carried out in a straightforward way without the need for sophisticated equipment. As we have demonstrated, it is effective. The energy consumption is low, since the only operation involved is addition of a slurry to the waste. Finally, the cost of the process is quite low. We shall have more to say about costs later.

The third approach to solving the coal waste problem is to collect and somehow treat all the effluents from the waste piles in order to render them harmless. There are a number of ways for doing this, including alkaline neutralization, ion exchange, reverse osmosis, use of chelating or complexing agents, freezing or distilling processes, biological treatment and the use of precipitating agents or selective adsorbents. We have examined most of these methods in order to determine their effectiveness, but the best of these is probably alkaline neutralization. This method is, in fact, the most widely used method for coal waste effluent control, probably because it is simple and easy

to implement. It has the additional advantages of being a proven technology and having a low cost.

Alkaline neutralization is carried out by simple addition of an alkaline material, usually hydrated lime, to the coal waste effluent. This has the effect of raising the pH into the neutral range and precipitating out most of the trace metals, which tend to be insoluble under these conditions. In principle one can calculate the concentrations of the trace metals in solution in such a system from thermodynamic considerations. We did this using a chemical equilibrium code (MINEQL).⁵ The results of these calculations, which are shown in Table 4, were then compared to the observed values from a coal waste leachate which had been neutralized to pH 6.49 with calcium hydroxide. Two things are clear from these results. First, all the elements examined are adequately controlled except for iron in the plus two oxidation state. Thus one should oxidize the iron before completing the treatment in order to prevent unacceptably large discharges of iron into the environment. The second point to note is that all of the measured values are lower, and sometimes substantially lower than the calculated values. This undoubtedly means that there are other processes, probably adsorption and entrapment phenomena, which limit the concentrations of the trace elements to values lower than those predicted by simple equilibrium models. It also means that the neutralization treatment of coal wastes effluents is even more effective than theory predicts.

Since alkaline neutralization does not deal with the real source of water pollution in these wastes, acid continues to be generated within the waste pile. Consequently treatment of the waste effluents must be continued as long as the waste pile has any acid generating capability. This may range into the hundreds of years. This single factor constitutes the major disadvantage to this approach to controlling coal waste effluents. An additional factor to consider is that one can never guarantee that all of the waste pile effluents are collected.

Table 5 shows some cost evaluations for a number of control options.⁶ These are in terms of March 1978 dollars for the three plants in the Illinois basin which we have sampled. It is clear that calcining of the coal waste is by far the most expensive option, with costs ranging from \$1.39/ton to \$9.89/ton. This treatment is clearly much too expensive to be of any value. The cost of lime/limestone slurry coating ranges from \$0.22/ton to \$0.50/ton and

is the cheapest treatment examined for Plant B. While these costs are quite reasonable, one must remember that the treatment is not permanent, and must be combined with some other disposal schemes, which will add to the overall cost. The cost of alkaline neutralization is the lowest for the other two plants examined, ranging from a low of \$0.066/ton to a high of \$0.55/ton. This would undoubtedly be the method of choice were it not for the requirement that the treatment be continued indefinitely.

CONCLUSIONS

Chemical and mineralogical examination of coal wastes and their drainages has lead us to consider three approaches to solution of the coal waste drainage problem. The first is alteration of the waste to render it non-polluting. Calcining of the waste has been shown to be an effective way of accomplishing this, but the cost of this technique is too high for it to be of any use. The second approach is codisposal of the coal waste with neutralizing and/or absorbing agents. The best way to implementing this approach is sequential slurry coating of the coal waste with lime and limestone, which is both effective and inexpensive. This is probably the best of the one-time treatments which we have evaluated when both effectiveness and cost are considered. Unfortunately this approach suffers from a lack of permanence and must be augmented with some other method of permanent disposal. The third approach to controlling coal waste effluents is to collect and treat the drainages. Perhaps the most effective way of doing this is by alkaline neutralization of the drainages. This is currently the most widely used technique for this purpose, because of its simplicity and availability. We have shown that it is effective provided that the iron is oxidized to the plus three oxidation state, and that the cost of this treatment is low. However, the need for continued treatment into the indefinite future must be considered a severe limitation.

REFERENCES

1. Wewerka, E. M., Williams, J. M., Wangen, L. E., Bertino, J. P., Wanek, P. L., Olsen, J. D., Thode, E. F. and Wagner, P., "Trace Element Characterization of Coal Wastes - Third Annual Progress Report," DOE LA-7831-PR, EPA-600/7-79-144 (June 1979).
2. Wewerka, E. M., Williams, J. M., Vanderborgh, N. E., Harmon, A. W., Wagner, P., Wanek, P. L. and Olsen, J. D., "Trace Element Characterization of Coal Wastes - Second Annual Progress Report," DOE LA-7360-PR, EPA-600/7-78-028a (July 1978).
3. Wewerka, E. M. and Williams, J. M., "Trace Element Characterization of Coal Wastes - First Annual Report," DOE LA-6835-PR, EPA-600/7-78-028 (March 1978).
4. Williams, J. M., Bertino, J. P., Jones, M. M., Wagner, P., Wanek, P. L., Wangen, L. E. and Wewerka, E. M., "Trace Element Characterization of Coal Wastes - Fourth Annual Progress Report," LA-8275-PR (In Press).
5. Heaton, R. C., Wangen, L. E., Wanek, P. L., Williams, J. M., Jones, M. M., Nyitray, A. M., Wagner, P. and Bertino, J. P., "Trace Element Characterization of Coal Wastes - Fifth Annual Report," LA-8826-PR (In Press).
6. Thode, E. F., Williams, J. M., Wewerka, E. M. and Wagner, P., "Cost of Coal and Electric Power Production - The Impact of Environmental Control Technologies for Coal-Cleaning Plants," LA-8039-MS (October 1979).

MEG/MATE ANALYSIS OF ILLINOIS-BASIN COAL WASTE LEACHATES

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

WORRY!
 E
 OK →

Fig. 1. MEG/MATE Analysis of Illinois Basin Coal Waste Leachates.

TABLE I
DISCHARGE SEVERITIES FOR SELECTED ELEMENTS
FROM HIGH SULFUR COAL WASTES

<u>PLANT</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>I</u>	<u>K</u>
AL	1.4	9.1	0.41	2.5	0.95
MN	5.2	4.4	2.6	1.2	2.0
FE	164	480	115	48	96
NI	27	43	26	4.9	4.8
CU	0.94	1.6	0.32	0.70	0.68
ZN	1.5	5.5	1.0	1.5	1.0
AS	0.03	1.4	0.14	0.64	0.44
CD	1.5	2.4	1.6	0.67	1.0
PH	2.9	1.7	2.4	2.3	2.1

^a Discharge Severity = Concentration / (100 x MATE)

TABLE II
AVERAGE MINERALOGY FOR COAL WASTES
FROM FIVE COAL PREPARATION PLANTS

<u>PLANT</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>I</u>	<u>K</u>
PYRITE	14	15	21	13	25
MARCASITE	8	11	9	0	0
QUARTZ	22	17	23	13	19
CALCITE	6	0	1	0	0
GYP SUM	3	1	1	1	1
ILLITE	14	11	16	9	16
KAOLINITE	15	7	14	7	10
MIXED CLAY	7	17	8	10	0
UNKNOWN				18	7
LTA				71.1	76.4

^aAll values in wt. percent based on the dry samples

TABLE III
TRACE ELEMENT LEACHABILITY OF A
HIGH-SULFUR COAL REFUSE SAMPLE
CALCINED AT 1000°C*

Element	Uncalcined Refuse (ppm)	Calcined Refuse (ppm)
Al	100	0.4
Fe	60 ^b	<0.03
Mn	5.6	0.02
Co	2.8	<0.01
Ni	4.8	0.01
Cu	0.10	0.0
Zn	2.8	0.05
Cd ^b	68 ^b	0.30
pH	2.0	8.0
TDS (%)	1.4	0.2

*Fig. Sources of refuse are refuse #1 and #2.

^bSee Table I, p. 10.

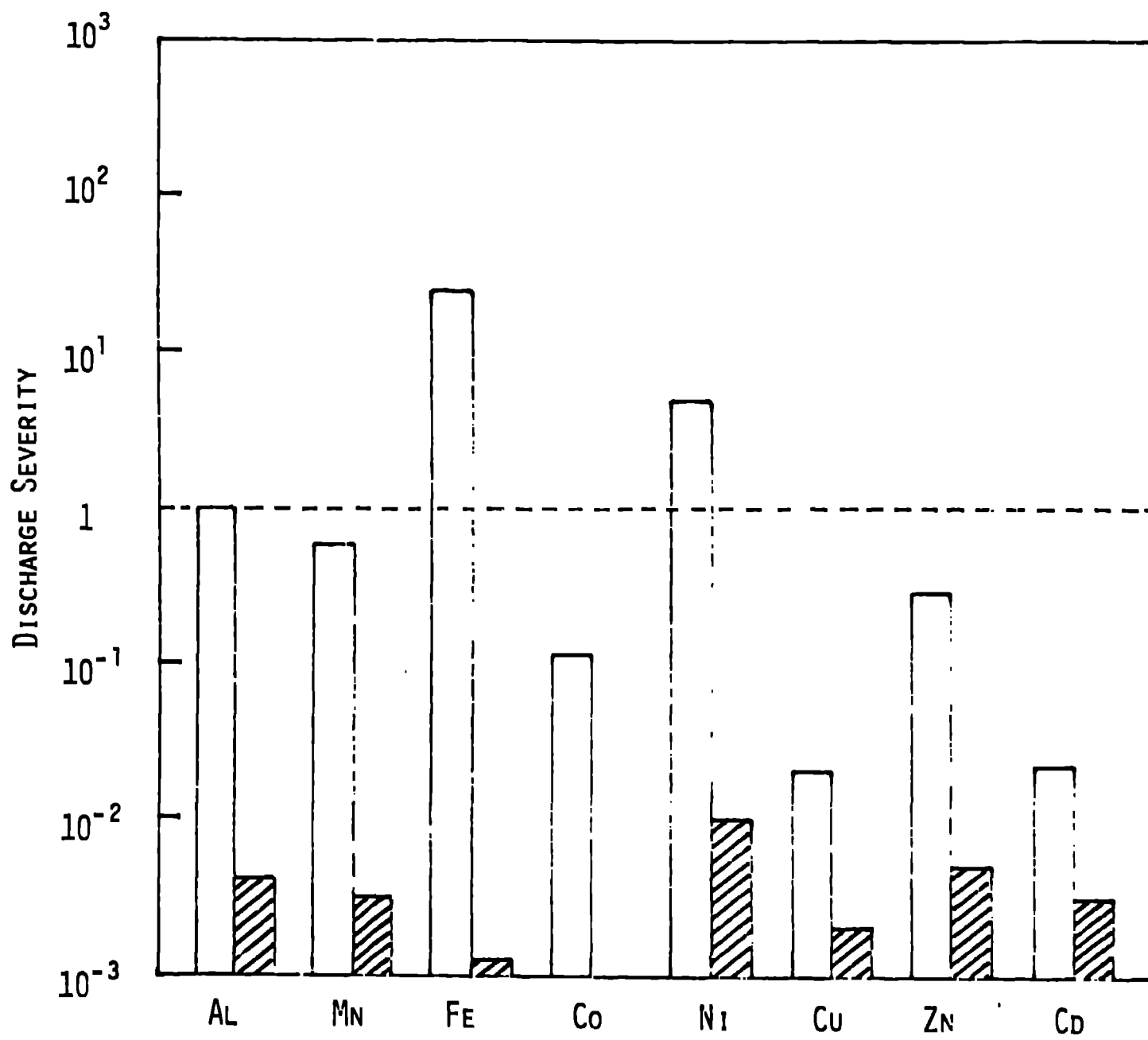


Fig. 2. Discharge Severities for Calced (shaded) and Untreated (unshaded) High Sulfur Coal Wastes.

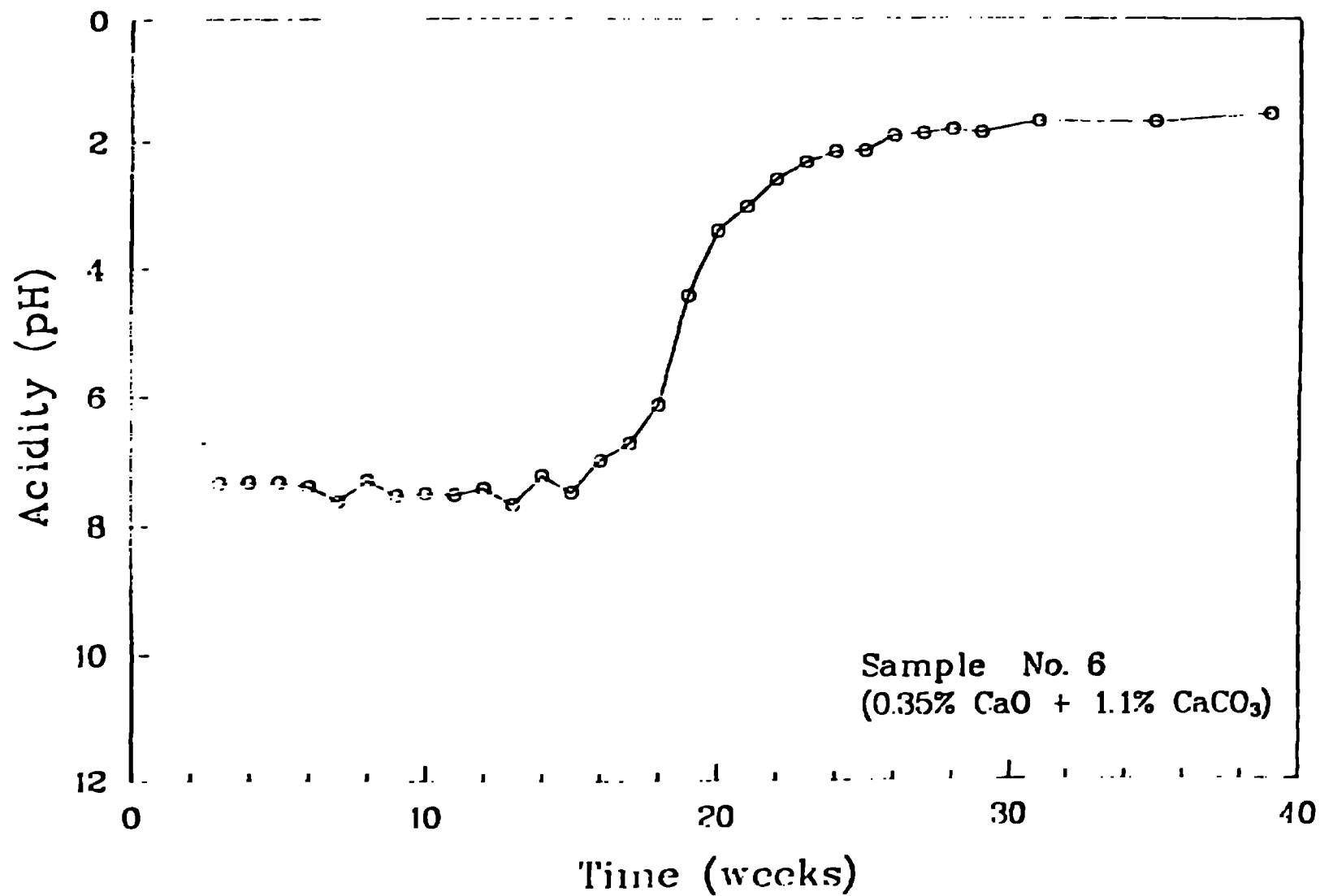


Fig. 3. Dependence of Effluent pH on Time for High Sulfur Coal Wastes Treated by Sequential Lime/Limestone Slurry Coating.

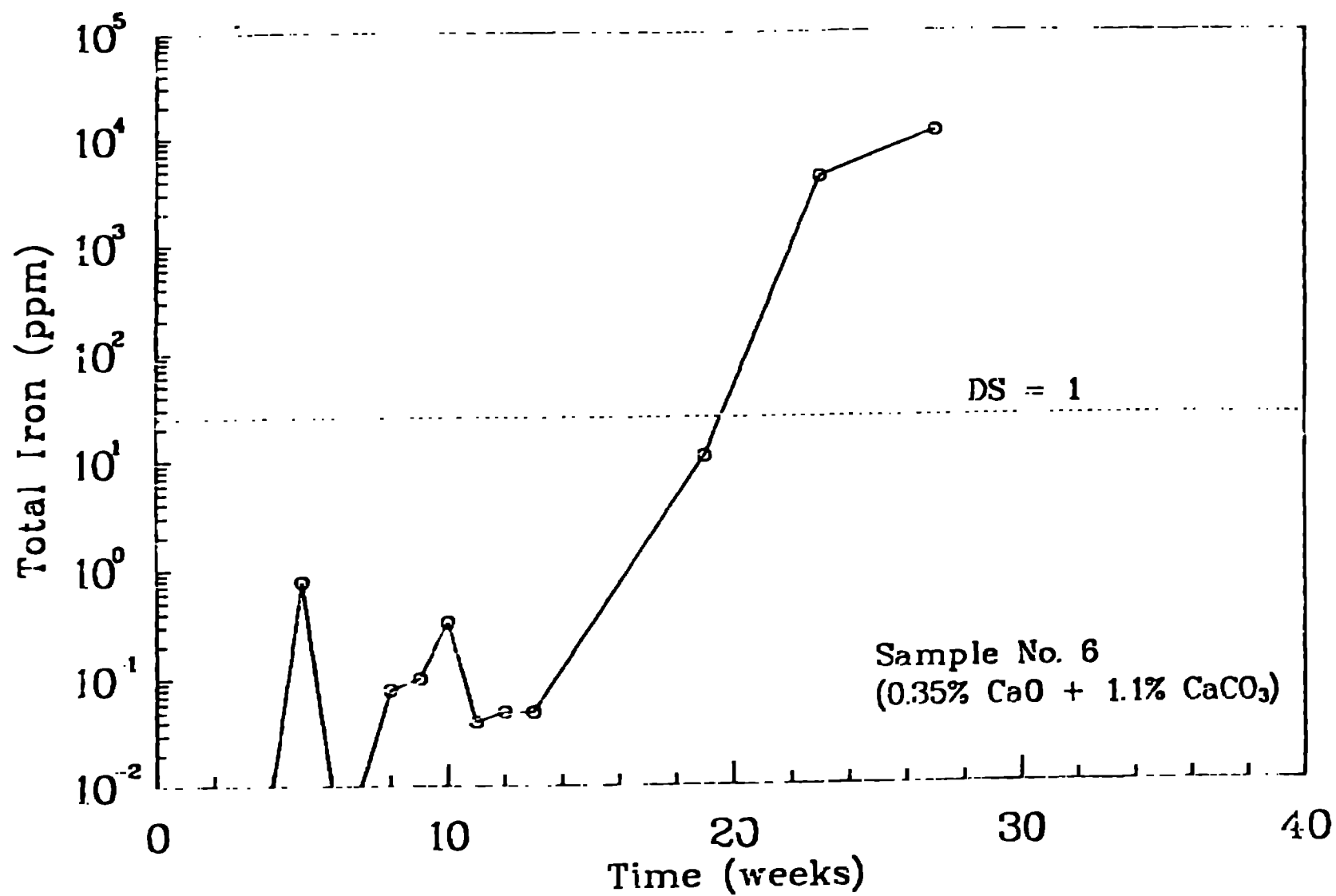


Fig. 4. Dependence of Effluent Iron Concentration on Time for High Sulfur Coal Waste Treated by Sequential Lime/Limestone Slurry Coating.

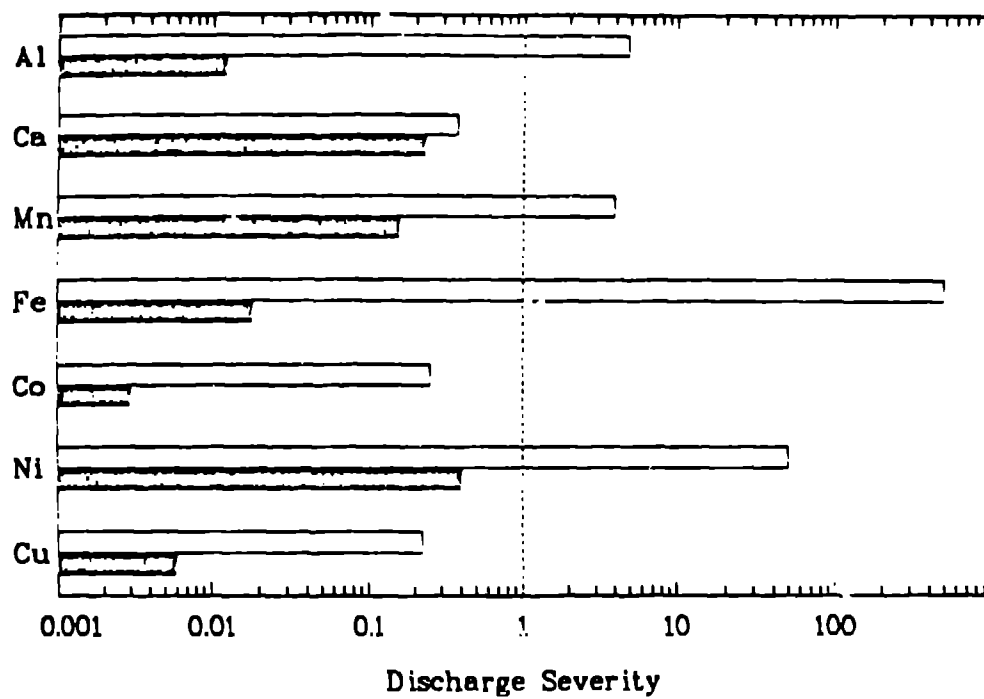


Fig. 5.
Discharge severities (leachate concentration/ $100 \times$ MATE) for selected trace elements in drainages from high-sulfur coal preparation wastes—untreated wastes (unshaded) and lime/limestone treated wastes (shaded).

TABLE IV
CALCULATED AND OBSERVED CONCENTRATIONS OF CHEMICAL
COMPONENTS IN COAL WASTE LEACHATES AFTER NEUTRALIZATION
TO PH 6.49 WITH CALCIUM HYDROXIDE

<u>ELEMENT</u>	<u>CALCULATED</u>	<u>OBSERVED</u>	<u>100(MATE)</u>
F	3.1	4.2	-
AL	0.002	<.1	100
CA	523	450	1600
CR	0.13	<.01	25
MN	9.9	8.1	10
FE(II)	1200	620] 25
FE(III)	0.0004	<.02	
Co	3.5	0.5	25
NI	7.5	0.5	1
CU	0.09	<.01	5
ZN	11.4	0.5	10
As(V)	0.76	<.02	5
CD	0.21	<.03	0.1

^a All values are in ppm

TABLE V

COSTS FOR VARIOUS ECT OPTIONS WITH COAL-CLEANING WASTE

Option	Cost (\$/ton of Product Coal)		
	Plant A(A)	Plant B(A)	Plant C(A)
1. Calcining, conventional FGD	8.30	3.40	9.89
2. Calcining, lime-limestone recycle system	3.36	1.39	3.99
3. Lime-limestone slurry coating	0.50	0.22	0.44
4. Direct addition of lime to pile*	1.91	0.45	1.33
5. Codisposal with alkaline soil	1.27	0.57	1.69
6. Codisposal with fly ash	5.84	2.62	7.71
7. Codisposal with limestone-modified fly ash	3.90	1.75	5.15
8a. Lime precipitation/clarification of effluent (first five years)	0.13	0.42	0.066
8b. Lime precipitation/clarification of effluent (last five years)	0.15	0.55	0.076
9. Reverse osmosis, effluent			0.26
10. Ion exchange, effluent			0.38

*Labor cost not included.